



Chapter (3)

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Thermochemistry

Introduction

All chemical reaction is accompanied by energy changes, this change appear in the form of evolution or absorption of heat. This branch of chemistry which deals with study of energy changes accompanying chemical reactions is termed as "Thermochemistry".

Thermochemistry is based on the first law of thermodynamics. The energy change in chemical reactions is largely due to change of bond energy (i.e. it results from the breaking of bonds in reactants and formation of new bonds in products).

Stander enthalpy change

As the enthalpy of reaction depends on temperature, a stander state is chosen to compare the enthalpies of reaction of different substances. A convenient stander state for a substance is the most stable under 1 atm and at the specified temperature (25°C or 298K).

For pure solids, liquids and ideal gases, the stander state corresponds to the state of the substance at 1 atm and specified temperature.

For the dissolved substances, the stander state of solute is that concentration which gives unit activity.

Stander enthalpy change

The stander enthalpy of reaction at a temperature T and a pressure 1 atm is donated by

$$\Delta H^{\circ} = \sum \Delta H^{\circ} \text{ products} - \sum \Delta H^{\circ} \text{ reactants.}$$

Enthalpy for every element in its stander state is zero.

For example:

The enthalpy for formation of a mole of CO_2 from its elements in the stander state is $-393.5 \text{ kJ.mol}^{-1}$.



The value of ΔH° is given as follows:

$$\Delta H^{\circ}_{298\text{K}} = H^{\circ}\text{co}_2 - [H^{\circ}\text{o}_2 + H^{\circ}\text{c}]$$

$$\text{At stander state } H^{\circ}\text{o}_2 = H^{\circ}\text{c} = 0$$

Hence, under these conditions

$$\Delta H^{\circ}_{298\text{K}} = H^{\circ}\text{co}_2 = -393.5 \text{ kJ.}$$

Heat of reaction

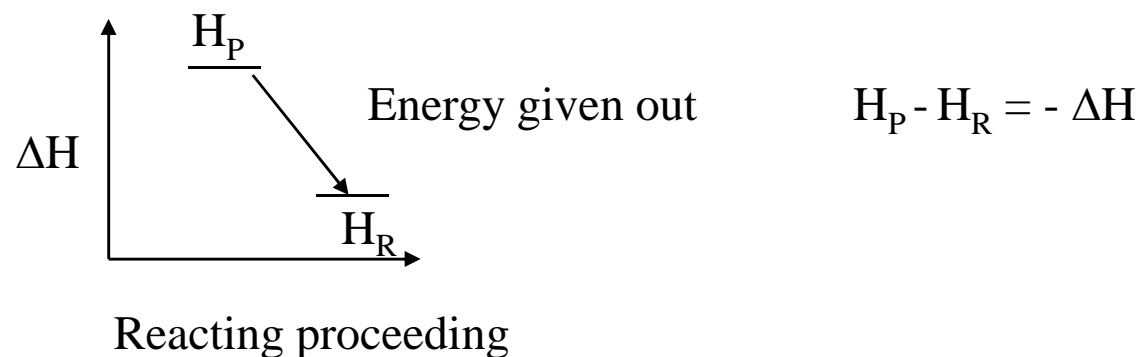
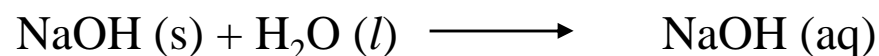
A reaction which proceeds with the evolution (give out heat) of heat is referred to as an

(a) exothermic reaction

In such reaction $H_R > H_P$, so that ΔH is negative.

In exothermic reaction, the total internal energy of reactants is more than that of products and therefore the excess of internal energy will appear ΔE is negative.

Example:



Heat of reaction

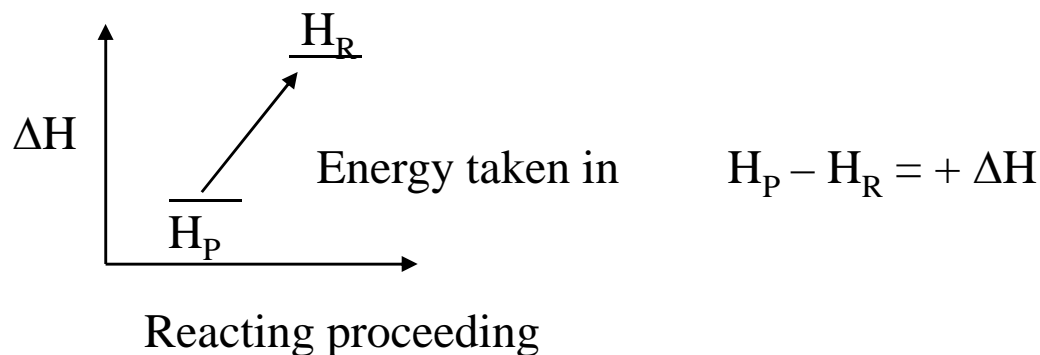
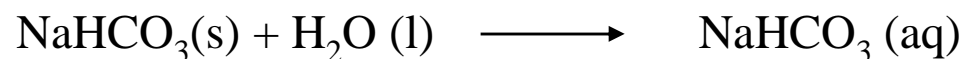
(b) Endothermic reaction

A reaction which proceeds with absorption of heat is referred to as an endothermic reaction.

In these reactions $H_P > H_R$, so that ΔH is positive.

In endothermic reaction, the total internal energy of products more than that of reactants and therefore the excess of internal energy will appear ΔE is positive.

Example



Relation between enthalpy and internal energy

Let consider a chemical reaction taking place at constant V and P, in such case $w=0$

$$\Delta U = q + w$$

$$\Delta U = q_V \dots\dots\dots(1)$$

And when pressure constant

$$\Delta H = q_P \dots\dots\dots(2)$$

The quantities ΔH and ΔU are related to each other by the expression

$$\Delta H = \Delta U + P\Delta V \dots\dots\dots(3)$$

Substituting eq.(1) and (2) in eq.(3), we get

$$q_P = q_V + P\Delta V \dots\dots\dots(4)$$

This relationship can be simplified as follows:

For n moles of an ideal gas

$$PV = nRT \dots\dots\dots(5)$$

Relation between enthalpy and internal energy

Let n_1 and n_2 represent the number of moles of gaseous reactants and products, suppose n_2 greater than n_1 $\Delta n_g = n_2 - n_1$. the corresponding increase in volume (ΔV) .

We can write eq.(5) by substituting Δn_g as follows:

$$P\Delta V = \Delta n_g RT \dots\dots\dots(6)$$

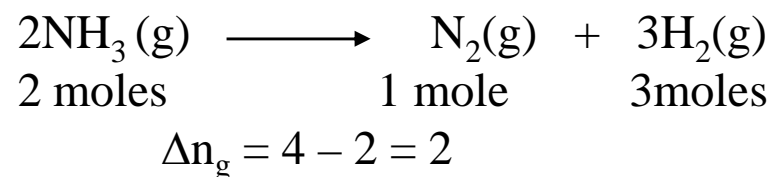
Substituting eq.(6) in eq.(4), we get

$$\mathbf{q_P = q_V + \Delta n_g RT \dots\dots\dots(7)}$$

Relation between enthalpy and internal energy

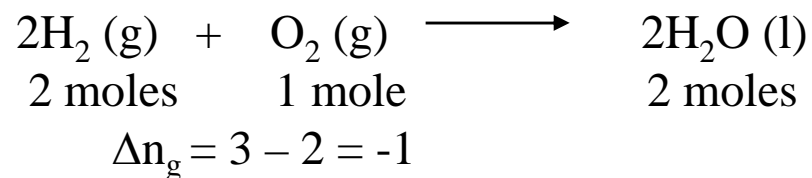
Example:

1. Reaction of the dissociation of ammonia into nitrogen and hydrogen



$$q_{\text{p}} = q_{\text{v}} + 2RT$$

2. In the reaction involving combination of hydrogen and oxygen.



$$q_{\text{p}} = q_{\text{v}} - RT$$

Laws of Thermochemistry

1) Lavoisier and Laplace's Law

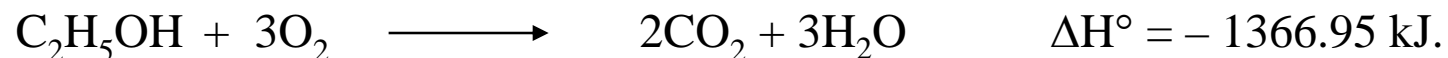
This law was given by Lavoisier and Laplace in 1780 and state of law as follows"

" The amount of heat supplied to decompose a compound into its elements is equal to the heat of formation of that compound from its elements“

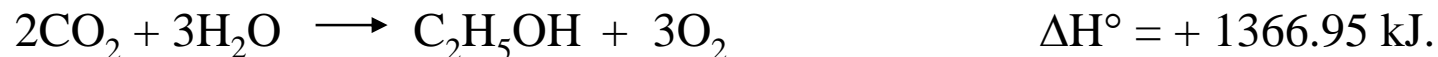
Means the heat of formation of compound is numerically equal to its heat of decomposition of a compound but of opposite sign.

The importance of this law is that thermochemical equations can be reversed.

For example:



Hence, by Lavoisier and Laplace's Law, we get



Laws of Thermochemistry

2) Hess's Law

State of Hess's Law as follows"

"The enthalpy change of a given chemical reaction is the same whether the process takes place in one or several steps".

Means heat of reaction does not depend upon the nature of intermediate products but depends only on the initial reactants and final products

.
For example: carbon dioxide may be produced by two processes which are:

First procedure:

The burning of carbon can take place in a single step to form CO₂ with the enthalpy change which is equal to -393.5 kJ



Laws of Thermochemistry

Second procedure:

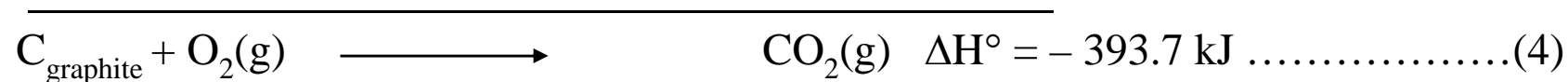
It is possible to carry out above reaction in two steps.

First, all carbon can be converted into carbon monoxide

Second, carbon monoxide can be oxidized to carbon dioxide as follows:



On adding eq.(2) and (3), we get



From eq.(1) and (4), it shows that the enthalpy change in both the procedures is almost same, The small difference due to experimental error.

Laws of Thermochemistry

Application of Hess's law

Hess's law gives mathematical method of calculating:

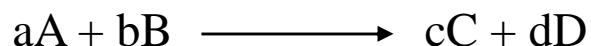
- i) Heat of Reaction
- ii) Heat of Transition
- iii) Heat of formation
- iv) Lattice Energy of Crystal

Laws of Thermochemistry

3) The Kirchhoff Equation (Variation of Enthalpy of a Reaction with Temperature):

The enthalpy changes of any process, whether physical or chemical varies with temperature. The exact influence of temperature can be worked out as follows:

The enthalpy change for the reaction



$$\text{is given by } \Delta H = \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}} = (cHC + dHD) - (aHA + bHB) \dots\dots\dots(1)$$

Differentiating eq.(1) with respect to temperature, keeping pressure constant, we get

$$[\partial(\Delta H)/\partial T]_P = c(\partial HC/\partial T)_P + d(\partial HD/\partial T)_P - a(\partial HA/\partial T)_P - b(\partial HB/\partial T)_P \dots\dots\dots(2)$$

$$= cC_p.C + dC_p.D - aC_p.A - bC_p.B = \Delta C_p \dots\dots\dots(3)$$

Laws of Thermochemistry

Where,

$$\Delta C_p = \text{Sum of heat capacities of products} - \text{Sum of heat capacities of reactants}$$

Eq.(3) is called Kirochhoff equation. It state that the variation of ΔH of a reaction with temperature at constant pressure is equal to ΔC_p of the system. We can get

$$d(\Delta H) = \Delta C_p dT \dots\dots\dots(4)$$

the temperature dependence of enthalpy of reaction at constant volume is given by

$$d(\Delta U) = \Delta C_v dT \dots\dots\dots(5)$$

Laws of Thermochemistry

if the temperature range of interest is small, eq.(4) and (5) can be easily integrated by assuming that heat capacities are independent of temperature. Accordingly

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P dT \quad \text{or} \quad \Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$$

Similarly

$$\int_{T_1}^{T_2} d(\Delta U) = \int_{T_1}^{T_2} \Delta C_V dT \quad \text{or} \quad \Delta U_2 - \Delta U_1 = \Delta C_V (T_2 - T_1)$$

Heat of Formation $\Delta H_f^\circ, \Delta H_f$

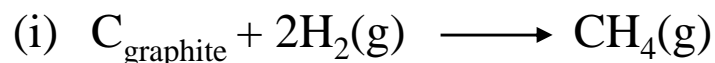
Enthalpy change when one mole of a substance is formed from its elements in their standard states. ΔH_f° value may be negative or positive.

$$\Delta H_f^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

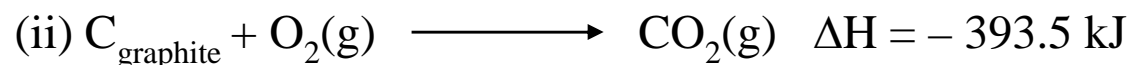
The heat formation of those compounds which cannot be determined experimentally can be calculated by Hess's Law.

For example:

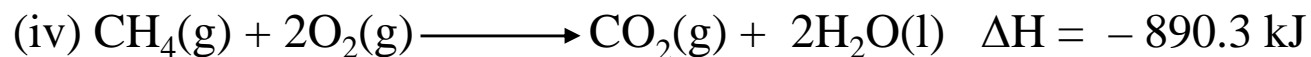
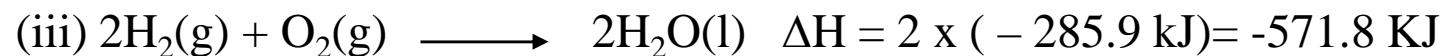
Enthalpy for formation methane from carbon graphite and hydrogen cannot be found directly as no chemical reaction occurs between graphite and hydrogen.



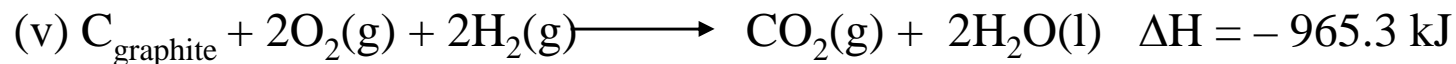
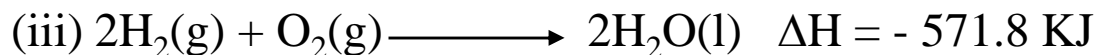
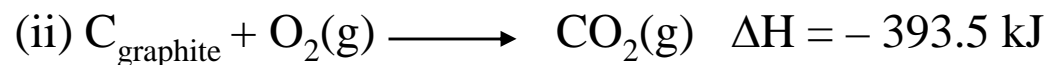
ΔH for above reaction may be calculated by the help of the following reactions:



Heat of Formation $\Delta H_f^\circ, \Delta H_f$

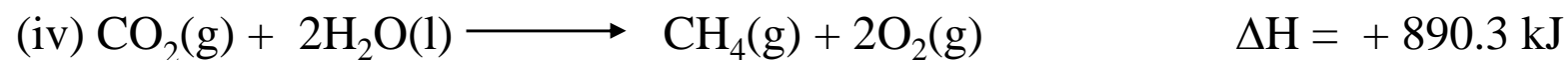


By adding eq.(ii) and (iii)



On subtracting reversed eq.(iv) from eq.(v), we obtain

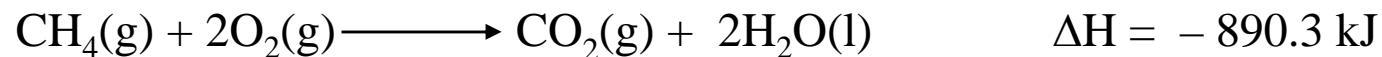
Heat of Formation $\Delta H_f^\circ, \Delta H_f$



Heat of Combustion ΔH_c

Defined as the enthalpy change accompanying complete combustion of one mole of substance at 25°C and 1 atm pressure.

For example:



Heat of Solution ΔH_s

Defined as the amount of heat evolved or absorbed when one mole of solute dissolved in a sufficient amount of the solvent.

When the dissolution of solute in a solvent is accompanied by enthalpy change of system. If the heat is absorbed from the solution ΔH_s is given a positive sign. If heat is evolved and given to solution ΔH_s is given a negative sign.

The enthalpy change when one mole of a solute is dissolved in a solvent to give a solution of a specified concentration is called integral enthalpy of solution. It depends on number of mole of solvent.

Heat of Solution ΔH_s

Table of

Integral Enthalpies of Solution in Water at 25°C

Substance	H ₂ O moles	Heat of Solution kJ mole ⁻¹
HCl	200	- 72.9
HBr	200	- 83.3
NH ₃	200	- 35.3
NaCl	200	+5.3
K ₂ SO ₄	400	+ 27.4
KCl	200	+ 18.6

It is clearly shown when the gases (HCl, HBr and NH₃) dissolved in water, ΔH has a negative value. (i.e. dissolution accompanied by evolution of heat. The dissolution of (KCl, NaCl and K₂SO₄) accompanied by absorbed of heat and their ΔH has a positive value.

Heat of solution ΔH_s

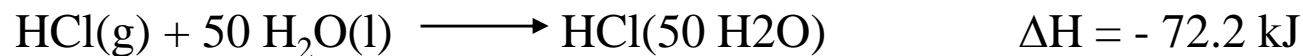
For example:

One mole of potassium chloride is dissolved in 200 moles of water, heat absorbed is 18.58kJ. the integral heat of solution of KCl at this concentration, expressed by a thermochemical equation as follows:



Similarly,

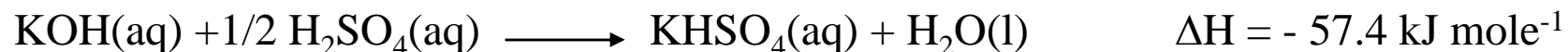
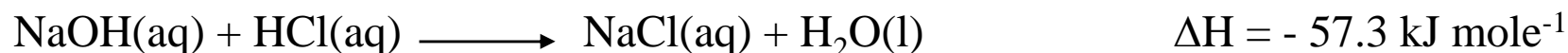
when 1 mole of gaseous hydrogen chloride dissolved in 50 moles of water, heat evolved is -72.2 kJ.



Heat of Neutralization ΔH_n

Enthalpy of neutralization of one mole of a strong base (such as NaOH and KOH) by a strong acid (such as HCl, H₂SO₄ and HNO₃) in dilute solution at 25°C and 1 atm pressure is called enthalpy of neutralization.

For example:



The neutralization of hydrochloric acid by sodium hydroxide in dilute solutions when acid reacted with alkali salt formed are completely dissociated, can be represented by



Or



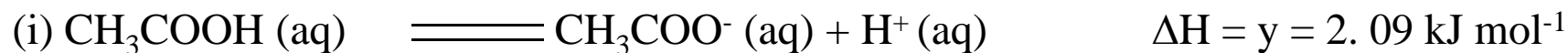
The neutralization reaction is the same as it simply involves the combination of H⁺ ions and OH⁻ ions to form unionized H₂O. the enthalpy of neutralization of all strong acid by a strong base and vice versa should be equal.

Heat of Neutralization ΔH_n

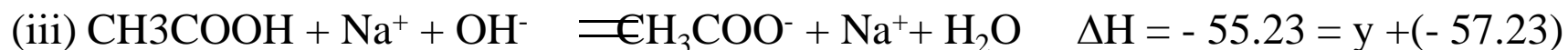
If the acid or base is weak, the enthalpy of neutralization is different because the reaction now involves dissociation of weak acid or weak base.

For example:

The neutralization of acetic acid by sodium hydroxide, involves the dissociation of acid as well as the usual neutralization of H^+ and OH^- ions. As represented below:



by adding eq.(i) and eq.(ii), we get



$$Y = 57.32 - 55.23 = +2.09 \text{ kJ mol}^{-1}$$

As H^+ ions neutralized by OH^- ions furnished by the completely dissociated sodium hydroxide. More H^+ ions formed by the dissociation of acetic acid to re-establish the equilibrium. Thus both reactions proceed side by side till acetic acid is completely neutralized.

The enthalpy of neutralization of acetic acid by sodium hydroxide found to be $\Delta H = -55.23$

$$\Delta H_{\text{acetic acid}} = +2.09 \text{ kJ mole}^{-1}$$

Heat of Neutralization ΔH_n

Table of

Standard Enthalpies of Neutralization of Strong Acid by Strong Base

Acid	Alkali	Enthalpy of Neutralization kJ mole ⁻¹
HCl	NaOH	- 57.32
HNO ₃	NaOH	- 57.28
HCl	KOH	- 57.45
HCl	LiOH	- 57.38

Bond Energy

The bond energy of a particular type of bond in a molecule may be defined as the amount of energy required to dissociate or break one mole of that type present in the compound and separate the resulting atoms or radical from one another.

For example:

The bond energy of the H-H bond in H_2 is 433 kJ mol^{-1} . it means that 433 kJ mol^{-1} of energy is required to break or dissociate the H-H bond in one mole of hydrogen molecules.

Bond Energy

Table of

Enthalpies of formation of bonds viz, bond energy at 25°C

Bond	Enthalpy of formation (kJ mol ⁻¹)
H – H	435.1
H – F	564.8
H – Cl	430.9
H – Br	368.2
O – O	138.1
O = O	493.7
O – H	464.4
C – H	416.2
C – O	351.4
C = O	711.3
C – C	347.3
C = C	615.0

Application of bond Energy

1) Determination of enthalpies of reactions

The bond energies can be used to determining enthalpies of reactions.

For example:

Determine the enthalpy of the reaction



In this reaction, the four C-H bonds of C_2H_4 remain unaffected. A double bond breaks in ethylene and an H-H bond breaks in H_2 , therefore one C-C and two C-H bonds are formed in C_2H_6 .

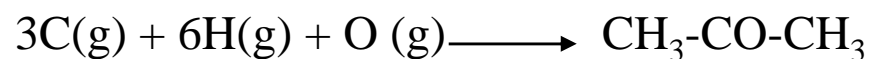
$$\Delta\text{H} = -\Delta\text{H}_{\text{C-C}} - 2\Delta\text{H}_{\text{C-H}} + \Delta\text{H}_{\text{C}=\text{C}} + \Delta\text{H}_{\text{H-H}}$$

$$\Delta\text{H} = -347.3 - 832.4 + 615 + 435.1 = -129.6 \text{ kJ mol}^{-1}$$

Application of bond Energy

2) Determination of enthalpies of formation of compound

For example: formation of acetone



I) Breaking 3H-H bonds to give six atoms of H, breaking of half O-O bond to give one atom of O and sublimation of 3C(s) to give three atoms of C(g).

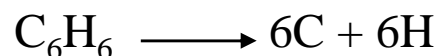
II) Formation of two C-C bonds, six C-H bonds and one C=O bond.

$$\begin{aligned}\Delta H_f &= -2\Delta H_{\text{C-C}} - 6\Delta H_{\text{C-H}} - \Delta H_{\text{C=O}} + 3\Delta H_{\text{H-H}} + 1/2\Delta H_{\text{O-O}} + 3\Delta H_{\text{C(s)} \rightarrow \text{C(g)}} \\ &= (-2 \times 347.3 - 6 \times 416.2 - 711.3) + (3 \times 435.1 + 1/2 \times 138.1 + 3 \times 719.6) \\ &= -369.95 \text{ kJ mol}^{-1}\end{aligned}$$

Application of bond Energy

3) Determination of resonance energy

For example:

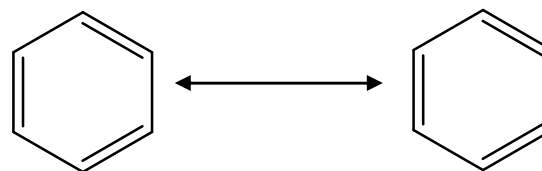


Benzene ring consists of three single and three double bonds (Kekule's structure), calculate the dissociation energy comes out as follows:

$$\begin{aligned}\Delta H_f &= 3\Delta H_{\text{C-C}} + 3\Delta H_{\text{C=C}} + 6\Delta H_{\text{C-H}} \\ &= 3 \times 347.3 + 3 \times 615.0 + 6 \times 416.2 = 5384.1 \text{ kJ mol}^{-1}\end{aligned}$$

The experimental value is known to be 5535.1 kJ mol⁻¹ but actual energy required for the dissociation of benzene is 151 kJ mol⁻¹ more than the calculate value. This clearly shows actual structure of benzene is more stable than Kekule structure by 151 kJ mol⁻¹

The actual structure represented as follows:



Factors effecting on Bond Energy

(a) Length of the bond

It is found the greater the bond length between the two nuclei of the two atoms forming

the bond, the smaller is bond energy.

Type of bond	H – H	Cl – Cl	I – I
Bond length	0.74	1.25	2.7
Bond energy	433.1	330.5	151.2

(b) Bond polarity

Greater is the strength of the dipole along the bond and higher is the bond energy.

Factors effecting on Bond Energy

(c) Unsaturation

It observe that with the increase in number of covalent bonds between atoms, increase in the bond energy

Bond	Energy in kJ/mol
C – C	347.3
C = C	615.0
C \equiv C	811.7

(d) Resonance effect

The bond energy per bond depends the amount of resonance.

(e) Overlap of orbital

The bond energy depends upon the s character which is determined by extent of overlap of orbital of the combining atoms.

Examples on Thermochemistry

Example (1)

One mole of naphthalene was burnt in oxygen gas at constant volume to give carbon dioxide gas and liquid water at 25°C. the heat evolved was found to be 5138.8 kJ. Calculate the enthalpy of reaction at constant pressure.

Example (2)

The enthalpy of combustion of glucose $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ is $-2816 \text{ kJ mol}^{-1}$ at 25°C . calculate $\Delta H^\circ_f (\text{C}_6\text{H}_{12}\text{O}_6(\text{s}))$. The ΔH°_f value for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -393.5 and $-285.9 \text{ kJ mol}^{-1}$.

Example (3)

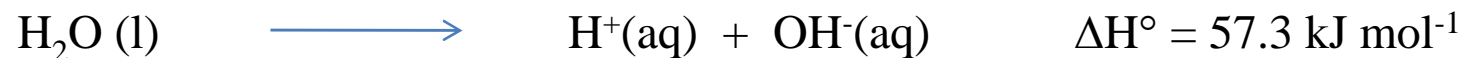
The heat evolved on dissolving $\text{CuSO}_4(\text{s})$ in water is 86.6 kJ mol^{-1} . If $\Delta H^\circ_f \text{Cu}^{+2}$ is 64.4 kJ mol^{-1} , what $\Delta H^\circ_f (\text{SO}_4^{-2})$. If $\Delta H^\circ_f \text{CuSO}_4(\text{s})$ is -770 kJ mol^{-1}

Example (4)

Cyanamid was subjected to combustion at constant volume and the heat evolved was found to be $742.7 \text{ kJ mol}^{-1}$ at 25°C . calculate q_v .

Example (5)

Calculate the enthalpy of formation OH^- ions at 25°C from the following thermochemical equations:



Example (6)

The enthalpy of reaction for the formation of ammonia according to reaction:

$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ at 27°C was found to be -91.94 kJ . What will be the enthalpy of reaction at 50°C ?

The molar heat capacities at constant pressure and 27°C for N_2 , H_2 and NH_3 are 28.45, 28.32 and 37.07 joules.

Example (7)

H.w

Calculate the enthalpy change at 125°C for the reaction.



The molar capacities (in $\text{J.K}^{-1} \cdot \text{mol}^{-1}$) for the various gases involved in the reaction vary with temperature as following:

$$C_p(\text{N}_2) = 27.26 + 5.23 \times 10^{-3} T - 4.18 \times 10^{-9} T^2$$

$$C_p(\text{H}_2) = 29.02 - 8.35 \times 10^{-4} T + 20.80 \times 10^{-7} T^2$$

$$C_p(\text{NH}_3) = 25.86 + 32.94 \times 10^{-4} T + 30.42 \times 10^{-7} T^2$$

Example (8)

How much heat is required to raise the temperature of one mole of oxygen from 300 K to 1300 K at constant pressure?

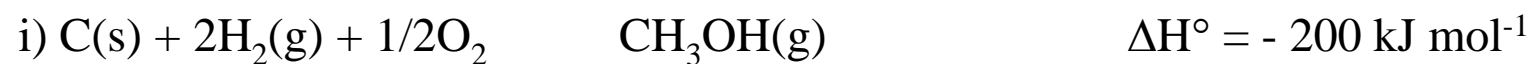
$$C_p = 6.095 + 3.253 \times 10^{-3} T - 1.017 \times 10^{-6} T^2$$

Example (9)

Heats of neutralization of NH_4OH and HF are -51.5 and 68.6 kJ mol^{-1} . Calculate heat of dissociation.

Example (10)

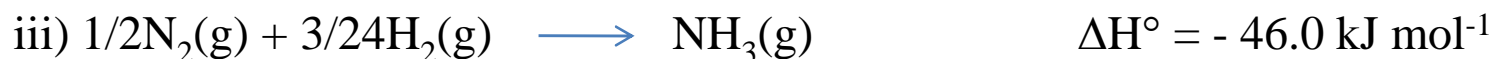
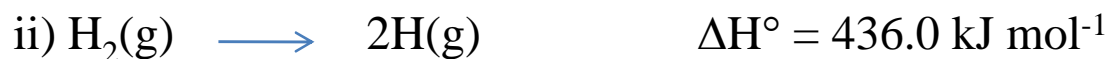
Calculate the bond enthalpy for a C – O band in methanol from the following data:



the bond enthalpy for C – H and O – H bonds are 413 and 463.6 kJ mol⁻¹.

Example (11)

The bond enthalpy of $\text{H}_2(\text{g})$ is 436 kJ mol^{-1} and that of $\text{N}_2(\text{g})$ is $941.3 \text{ kJ mol}^{-1}$. Calculate the average bond enthalpy and N – H in ammonia $\Delta H^\circ_f = -46.0 \text{ kJ mol}^{-1}$



Thanks for your attention

